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Optimization of Zone Refining by Variable Oscillation of the Container

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Abstract

A zone refining apparatus able to provide a wide range of rotation and oscillation programs is presented, and its utility in determining the conditions for most efficient separation is demonstrated.

INTRODUCTION

Zone refining is a powerful method for obtaining highly pure materials. Several comprehensive texts describing it and allied techniques are available (1, 2). While inorganic materials have been the most common substrates, a sizable body of literature discusses applications involving organic materials (3).

The efficiency of the process (4) is of prime concern to the user and has been treated by a number of workers. For example, Gouw and Jentoft (5) have evaluated the efficiencies of normal freezing, column crystallization, and zone melting. Pospisil (6) has attempted to formulate a method for predicting the optimum rate of zone travel. Kirgintsev and Avvakumov (7) have evaluated the efficiency of zone refining of fused salt systems in terms of the rate of crystallization, while Konovalov and Peizulaev (8) have presented a method for calculating the optimum conditions for the concentration of impurities in bismuth. Optimization with respect to the overall economics of the process has been treated by Kirgintsev and

Pyl'neva (9). Operating conditions can have a dramatic effect upon the separation. It is well known that stirring the molten zone will improve the separation by decreasing δ , the thickness of the diffusion layer. Yoshida et al. (10) and Avramenko et al. (11) have clearly demonstrated that zone refining processes can be optimized with respect to this operating variable. In this report a zone refining apparatus will be described which makes use of recent advances in integrated circuit technology in order to provide a very wide range of oscillation programs. The time between reversal of rotation at which the separation is most effective will likely depend upon the characteristics of the particular system. Using a very simply derived criterion for efficiency, the utility of this device will be demonstrated. Additionally, a method for obtaining a useful first approximation to the optimal zone travel rate will be described. The model system used was acetanilide containing approximately 0.01% methyl violet.

EXPERIMENTAL

Description of Apparatus

The basic circuitry of the zone refiner is depicted in Fig. 1. The device can accommodate four tubes and has four ovens, in sequence, for each tube. The table on which the ovens and cooling rings are mounted is driven by a threaded rod which is attached to a transmission gear assembly. As a pass is completed, the table reverse microswitch is tripped and an electromagnet (a) shifts the transmission gears so that the direction of table motion is reversed, and (b) increases the table transport motor speed. The table will then hit a backstop, return the microswitch to its original position, and begin a new pass. A toggle switch on the panel allows the operator to select either single pass or continuous operation.

The oscillation control logic is depicted in Fig. 2. The four rod holders are connected by a toothed belt to the stepping motor (Superior Electric, Bristol, Connecticut). The STM 101 stepping motor control (Superior Electric) accepts digital pulses from the logic circuit and emits pulses compatible with the stepping motor. Using the selector switch on the panel, the operator can select continuous rotation, oscillation, or stationary modes. A stepping motor rotates in discrete steps, each step being equivalent to 1.8° . Speed is specified in steps per second. Two 10-turn potentiometers are provided for this purpose, one to specify clockwise speed and the other counterclockwise speed. The Datel V/F 10 KIC chip (Datel Corp., Mansfield, Massachusetts) provides the memory required for

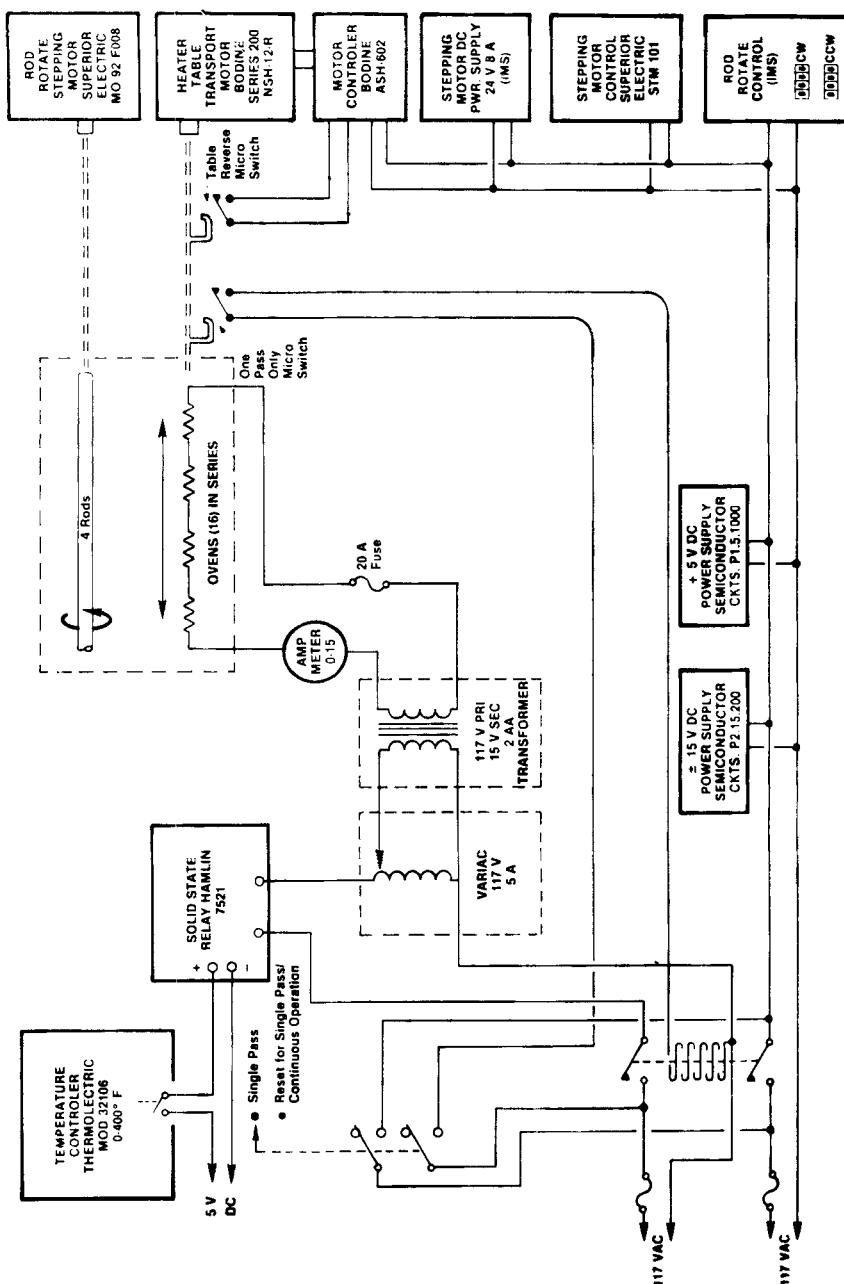


FIG. 1. Basic circuitry of the zone refiner.

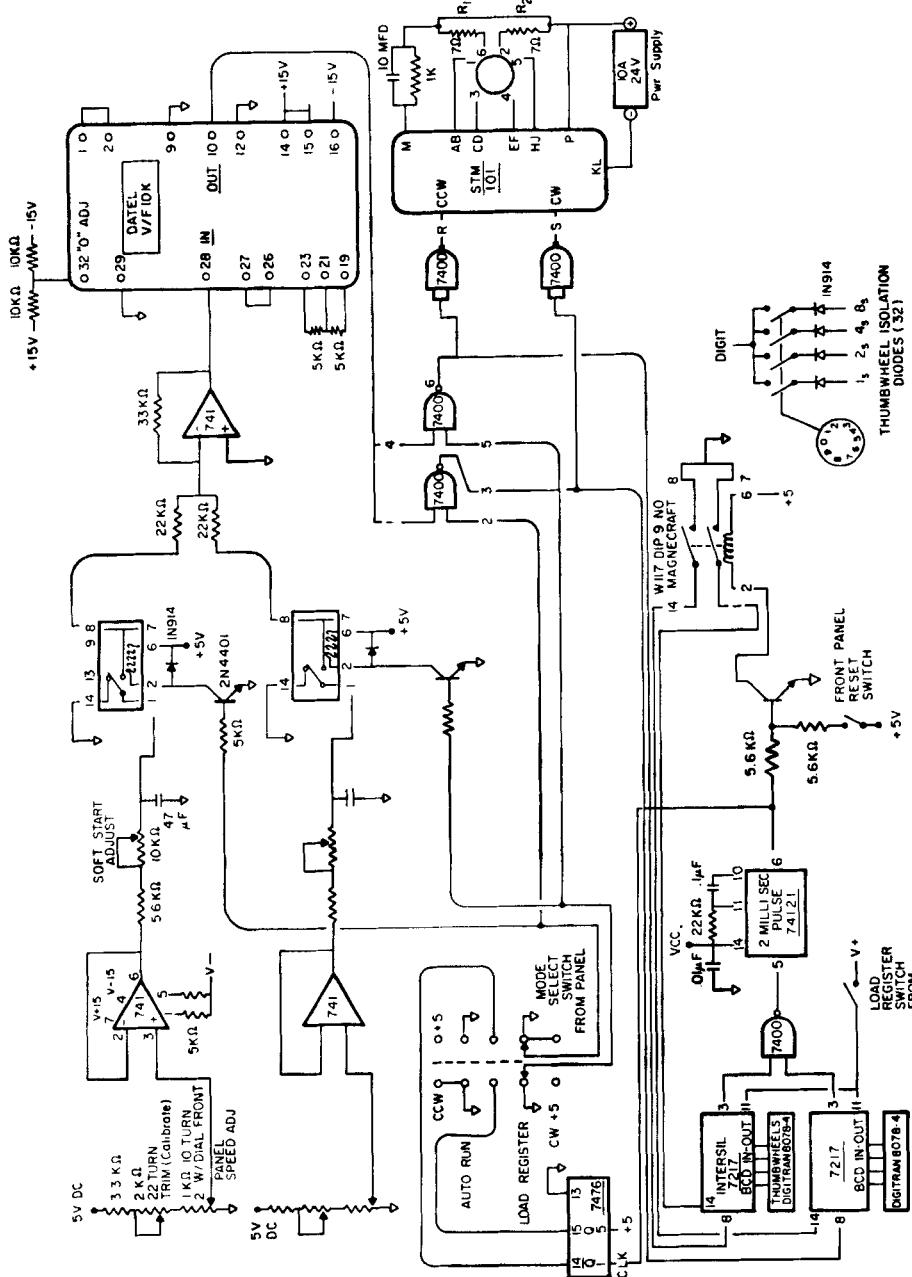


FIG. 2. Oscillation control logic circuitry.

oscillation. Two sets of thumbwheels, each 0-9999, determine the number of steps the rods will rotate in each direction. The Datel chip counts the steps, determines when the preset maximum has occurred, and then reverses direction. Thus a wide variety of oscillation programs can be obtained by varying both the speed and duration of rotation separately for each direction.

Materials and Methods

Acetanilide (97%; Aldrich Chemical Co., Milwaukee, Wisconsin) was twice recrystallized from water and stored under vacuum. Methyl violet (indicator grade) was dissolved in molten acetanilide to form a 0.01% (by weight) solution. Pyrex glass tubes (4 mm) were passed through a flame in order to evaporate adsorbed water and thereby reduce bubble formation, and the molten acetanilide solution was drawn into the tubes. The molten zone length was kept constant at 1.0 cm. For each stirring mode, several runs were made at each of two zone travel rates, 4.65 and 12.0 cm/hr. When the oscillation program was such that the tube made less than a full turn before reversal, the zone refiner was set so that the clockwise period was very slightly greater than the counterclockwise so as to compensate for any thermal variations. Rotation speed was maintained at 1000 steps per second. After one zone pass, each tube was analyzed spectrophotometrically at 580 nm. The effective distribution coefficient, k_e , was determined using (12)

$$\frac{C_x}{C_0} = 1 - (1 - k_e) e^{-k_e x/l} \quad (1)$$

where C_x is solute concentration at distance x , C_0 is the original solute concentration, and l is molten zone length. This equation was rearranged to give a form more convenient for plotting:

$$\ln \left(1 - \frac{C_x}{C_0} \right) = \ln (1 - k_e) - \frac{k_e x}{l} \quad (2)$$

RESULTS AND DISCUSSION

Values for the effective distribution coefficient, k_e , were obtained for a range of oscillation programs at two zone travel rates, 4.65 and 12.0 cm/hr. The reciprocal of k_e can be taken as one measure of the effectiveness of the separation, and this term has been plotted vs t , the time between

reversal of rotation, in Fig. 3. It is clear that the best separation is achieved when $t = 0.03$ sec. This graph, however, does not give any basis for comparing the results at the two zone travel rates.

A simple method to calculate efficiency will be described here that is applicable to the single pass zone refining of a semi-infinite rod. For a given experiment, where k_e and zone travel rate, f , are known, the efficiency will be defined as the amount of material produced for which the ratio C/C_0 is at or below a certain value, P , the desired purity, divided by the amount of time required to produce it. Here it is assumed that k_e and P are always less than unity. The "amount of material" will be represented by the shaded area in Fig. 4. Rearranging Eq. (1) and substituting our chosen value of P for C/C_0 , we get Eq. (3) and a value for x' :

$$x' = -(l/k_e) \ln [(1 - P)/(1 - k_e)] \quad (3)$$

If we integrate Eq. (1) with respect to x , evaluate between x' and zero, subtract the result from x' , and also subtract the area above the P line,

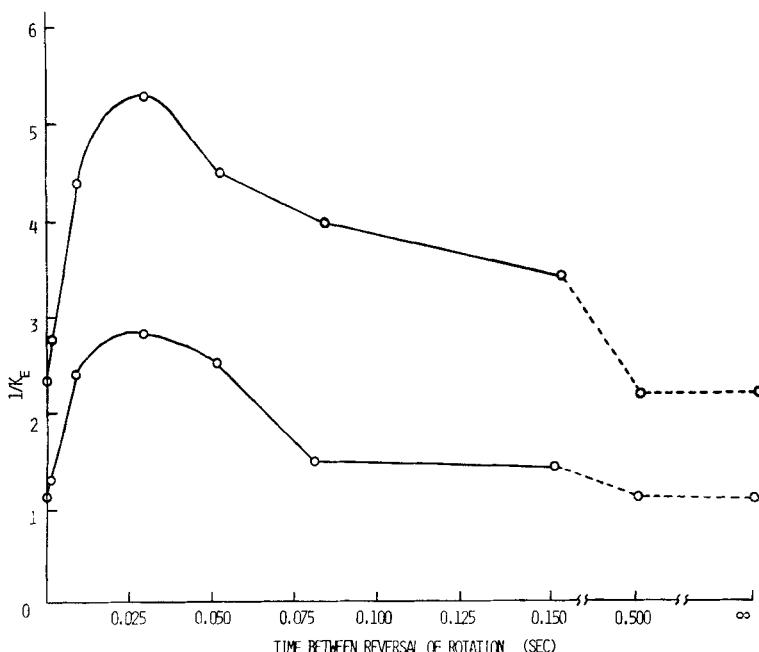


FIG. 3. $1/k_e$ vs time between reversal of rotation for two zone travel rates.
Top: 4.65 cm/hr.
Bottom: 12.0 cm/hr.

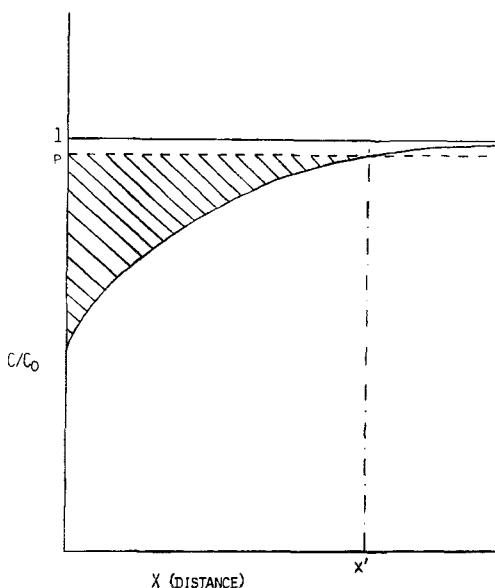


FIG. 4. Hypothetical C_x/C_0 vs distance after one zone pass.

equal to $(1 - P)x'$, we get Eq. (4) which describes the shaded area:

$$\text{Area} = (P - 1)x' + \frac{(1 - k_e)l}{k_e} [1 - e^{-k_e x' / l}] \quad (4)$$

Finally, dividing Eq. (4) by time, equivalent to x'/f , we obtain an expression for efficiency as a function of k_e and f :

$$\text{Efficiency} = f(P - 1) + \frac{(1 - k_e)lf}{k_e x'} [1 - e^{-k_e x' / l}] \quad (5)$$

Values for the efficiency at the two zone travel rates were calculated using Eq. (5) and plotted vs t , as shown in Fig. 5. This graph gives more useful information than that in Fig. 3. Not only does it show that $t = 0.03$ sec is most effective for this system, but also that it is more than twice as efficient to run at $f = 12.0$ cm/hr than at $f = 4.65$ cm/hr. The optimum zone travel rate could be found by plotting E vs f . This would require that k_e be known as a function of f . Burton et al. (13) related k_e to f by means of two constants: k_0 , the equilibrium interfacial distribution coefficient, and δ/D , the diffusion layer thickness over the diffusion constant:

$$k_e = 1/[1 + (1/k_0 - 1)e^{-f\delta/D}] \quad (6)$$

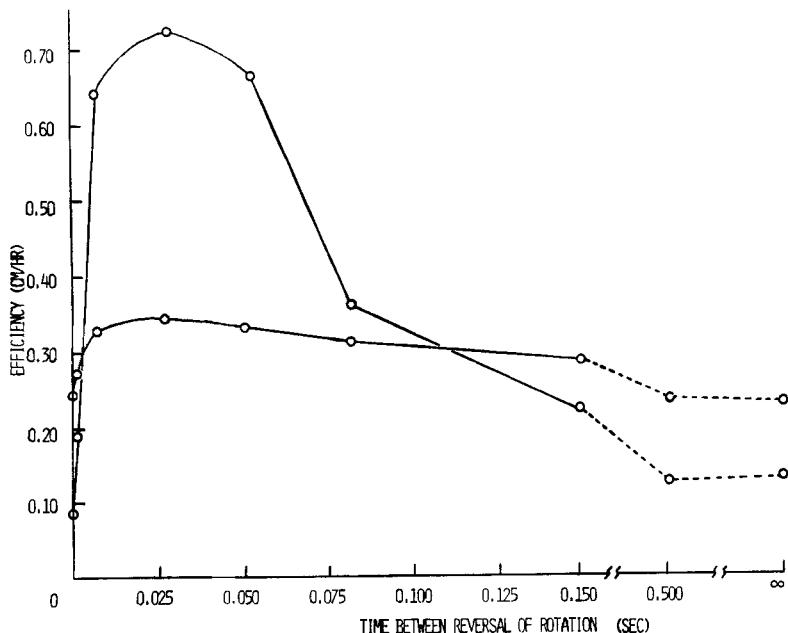


FIG. 5. Efficiency vs time between reversal of rotation for two zone travel rates. Top: 4.65 cm/hr. Bottom: 12.0 cm/hr.

If this equation was strictly valid, k_0 and δ/D could be calculated using k_e values obtained at two zone travel rates under the same oscillation conditions. Then one could obtain k_e , and by Eq. (5) get E for any zone travel rate, easily finding the optimum rate. Kirwan (14-17) has shown, however, that above a critical crystallization rate the planar interface breaks down to a cellular or dendritic interface, resulting in the trapping of impurity-rich liquid droplets. Then k_0 in Eq. (6) must be replaced by an apparent interfacial distribution coefficient, k_a , where for organic systems

$$k_a = 1 - A_1^2 \left[\frac{k_0 D}{m C_L(\infty) f} \right] \quad (7)$$

where A_1 is a constant, m is the liquidus slope, $C_L(\infty)$ is the impurity concentration in the bulk of the liquid, and the other terms have been previously defined. While the occurrence of interfacial breakdown precludes an exact mathematical solution for the optimum rate, a very useful first approximation to this quantity can be obtained using Eq. (6) by the

TABLE I
Approximate Optimum Rate Values for Selected Oscillation Conditions

Time between reversal of rotation (sec)	Approximate optimum rate (cm/hr)
0	5.5
0.010	16.4
0.030	18.6
0.050	16.9
0.080	9.2
∞	6.2

procedure outlined above. The approximate optimum rate values calculated are given in Table 1. One would expect that the actual optimum rates would be somewhat lower than these first approximations due to the occurrence of impurity trapping.

In summary, this device has been found to be very useful in determining the optimum oscillation conditions and in obtaining an approximation to the optimum zone travel rate. The numerical values found are very likely valid only for the particular system at hand, and this general procedure would have to be carried out in order to determine the optimum conditions for other separations.

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